GLC Flavor Profile of Maple Sirup

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Studies during the past several years on the flavorants of maple sirup have led to the development of a GLC procedure that produces a chromatogram representing a flavor profile of maple sirup. The analysis of numerous maple sirups from different regions of the maple belt shows that the geographic location of maple trees does not qualitatively affect the major flavorants of maple sirup.

Techniques for the isolation and identification of the flavorants of maple sirup have been described (1–6). Previous studies showed that chloroform completely removes the flavoring compounds from maple sirup, and that the chloroform flavor extract is free of the sugars of the sirup. GLC proved to be the most effective technique for separating the many compounds in this chloroform extract. Several different types of columns as well as different sets of operating conditions were necessary to obtain pure fractions for identification tests by infrared absorption and mass spectrographic analysis. Different GLC operating conditions were employed for the lower boiling components than for the higher boiling ones (2, 5, 6).

A method to evaluate maple flavor is needed in the maple sirup industry. Such a method would be useful in determining the quality of maple products and as an aid in detecting adulteration. With the objective of developing such a method the Associate Referee initiated studies to determine the GLC conditions under which a single chromatogram could be obtained to show the flavorants of maple sirup. The results of these studies are reported in this paper.

Experimental

Apparatus and Reagents

(a) *Gas chromatograph.*—An F & M Model 720 chromatograph was used in this study with the following conditions: *Column:* dual, stainless steel, ¼″ od × 4′. *Packing:* 20% Carbowax 20M on 60–80 mesh, acid-washed Chromosorb W *Detector:* thermal conductivity. *Temperatures:* injector port 145°C, column oven 50°C for 4 mm, 50–240°C at ca 3.5°/min (56 min), detector 250°C. *Helium flow:* 50 ml/min. *Attenuation:* 4×.

(b) *Shaker.*—Box-type.

(c) *Sintered glass filter.*—Coarse porosity, 3″ diameter.

Procedure

Extraction of flavorants.—Two quarts of the sirup to be tested were placed in a gallon jug or bottle, 1000 ml chloroform was added, and the container was stoppered tightly and shaken continuously 30 min at moderate speed. (*Caution:* Too rapid shaking caused the formation of a stable emulsion.) The sirup-chloroform mixture was transferred into a separatory funnel and allowed to stand until the sirup and chloroform separated.

The chloroform layer was removed and the sirup returned to the shaking container. The extraction was repeated with a second 1000 ml portion of chloroform. The combined extracts were allowed to evaporate to 100 ml at ambient temperature in a fume hood through which a current of air was passing. Then 400 ml diethyl ether was added to this concentrate and any precipitate formed was separated by filtering the solution through a coarse sintered glass filter funnel. The ether-chloroform filtrate was air-evaporated, as above, to 5 ml. The concentrate was stored in a glass-stoppered bottle for gas chromatographic analysis.

Gas chromatographic flavor profiles.—A 500 µl portion of the flavor concentrate was injected into the GLC instrument set at the operating conditions described above. The resulting chromatogram represented a GLC flavor profile of the sirup.

Results and Discussion

The GLC flavor profile for a fancy grade maple sirup is shown in Fig. 1. The more important flavor compounds indicated by the peaks are acetol (*1*), isomaltol (*9*), cyclotene (*11*), α-furanone (*17*), hydroxymethylfurfural (*22*), vanillin (*23*), syringaldehyde (*24*), and

[1] Deceased.

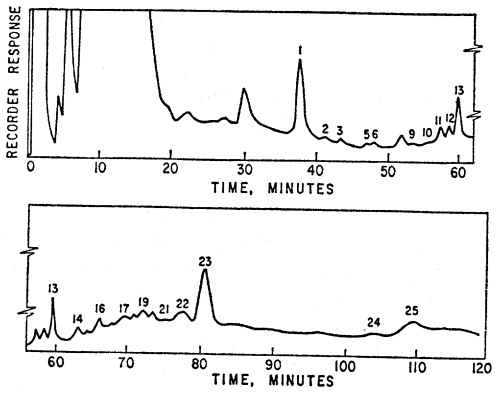

FIG. 1—GLC flavor profile of a typical fancy grade commercial maple sirup.

dihydroconiferyl alcohol (*25*). As earlier work (7) had shown that acetol and vanillin are present in sirup in an amount equal to only a few parts per million, the small peaks represent only traces of compounds. Also this chloroform extract contains compounds at levels too low to be indicated on this chromatogram. These have been separated and identified by different techniques previously.

Profiles were determined for fancy grade maple sirups from five different maple sirup-producing areas in the United States. All of the profiles contained better than 90% of the total peaks shown in Fig. 1. A summary of these is shown in Table 1. Those components listed by name were identified in earlier reports (1–3, 5, 6). The relative amounts of each constituent are indicated by peak heights in millimeters. These values are not necessarily quantitative since relatively large experimental errors were possible due to the extensive concentration made in the preparation of the extracts for the chromatographic analysis. The accuracy and precision of these values will have to be determined before the procedure can be used to detect adulteration. Also, natural variation in the amounts of significant constituents must be determined.

The profiles show that the chloroform flavor extract of maple sirup is remarkably uniform regardless of the geographic location where the sirup was made or by whom it was made. Thus, this profile offers great potential for determining the quality of the flavor of maple sirup and in detecting adulteration.

Table 1. Peak heights[a] of components of maple sirup flavor extract

Peak No.	Identity	Sirup 1	2	3	4	5
1	Acetol	19	8.0	45	10	21
2		—	—	—	—	—
3	Acetic acid	3.0	2.0	0.5	2.0	2.0
4		0.5	—	—	—	—
5	Propionic acid	0.5	2.5	0.5	0.5	1.5
6		4.5	1.5	1.0	3.5	2.0
7	*n*-Butyric acid	0.5	1.0	0.5	0.5	1.0
8	Furfural	2.0	0.5	1.5	0.5	0.5
9	Isomaltol	—	0.5	1.0	1.5	0.5
10		1.0	0.5	0.5	1.0	0.5
11	Cyclotene	4.5	2.0	5.5	1.5	4.5
12		30	—	—	1.0	—
13	BHT[b]	24	19	28	18	13
14		5.5	2.5	7	3.0	4.5
15		—	—	0.5	2.5	2.0
16		1.5	4.5	4.0	2.0	5.0
17	α-Furanone	2.5	—	1.0	2.0	0.5
18		4.0	1.5	0.5	0.5	1.0
19		2.5	2.0	3.0	2.5	1.5
20		1.5	2.5	1.5	2.5	1.5
21		0.5	1.0	3.0	2.0	2.0
22	Hydroxymethylfurfural	4.0	2.5	3.0	6.0	4.0
23	Vanillin	38	14	83	85	48
24	Syringaldehyde[c]					
25	Dihydroconiferyl alcohol[c]					

[a] In millimeters.
[b] Artifact introduced by diethyl ether treatment of extract.
[c] Peaks are too low and broad for heights to have any significance.

To increase the usefulness of this profile, work is now being done to modify the procedure so that the highly sensitive GLC flame ionization detector can be used. This would make possible the use of much smaller sirup samples and volume of solvent. In addition, other solvents will be tested. The results of these studies as well as the effect of experimental factors on the results will be given in a subsequent report.

This report of the Associate Referee, J. C. Underwood, was presented at the 82nd Annual Meeting of the Association of Official Analytical Chemists, Oct. 14–17, 1968, at Washington, D.C.

References

(1) Underwood, J. C., Willits, C. O., and Lento, H. G., *J. Food Sci.* **26**, 288–290 (1961).
(2) Underwood, J. C., and Filipic, V. J., *This Journal* **46**, 334–337 (1963).
(3) Filipic, V. J., and Underwood, J. C., *J. Food Sci.* **29**, 464–468 (1964).
(4) Underwood, J. C., and Filipic, V. J., *ibid.* **29**, 814–818 (1964).
(5) Filipic, V. J., Underwood, J. C., and Willits, C. O., *ibid.* **30**, 1008–1015 (1965).
(6) Underwood, J. C., and Filipic, V. J., *This Journal* **48**, 689–693 (1965).
(7) Filipic, V. J., Underwood, J. C., and Dooley, C. J., *J Food Sci.* (in press).